

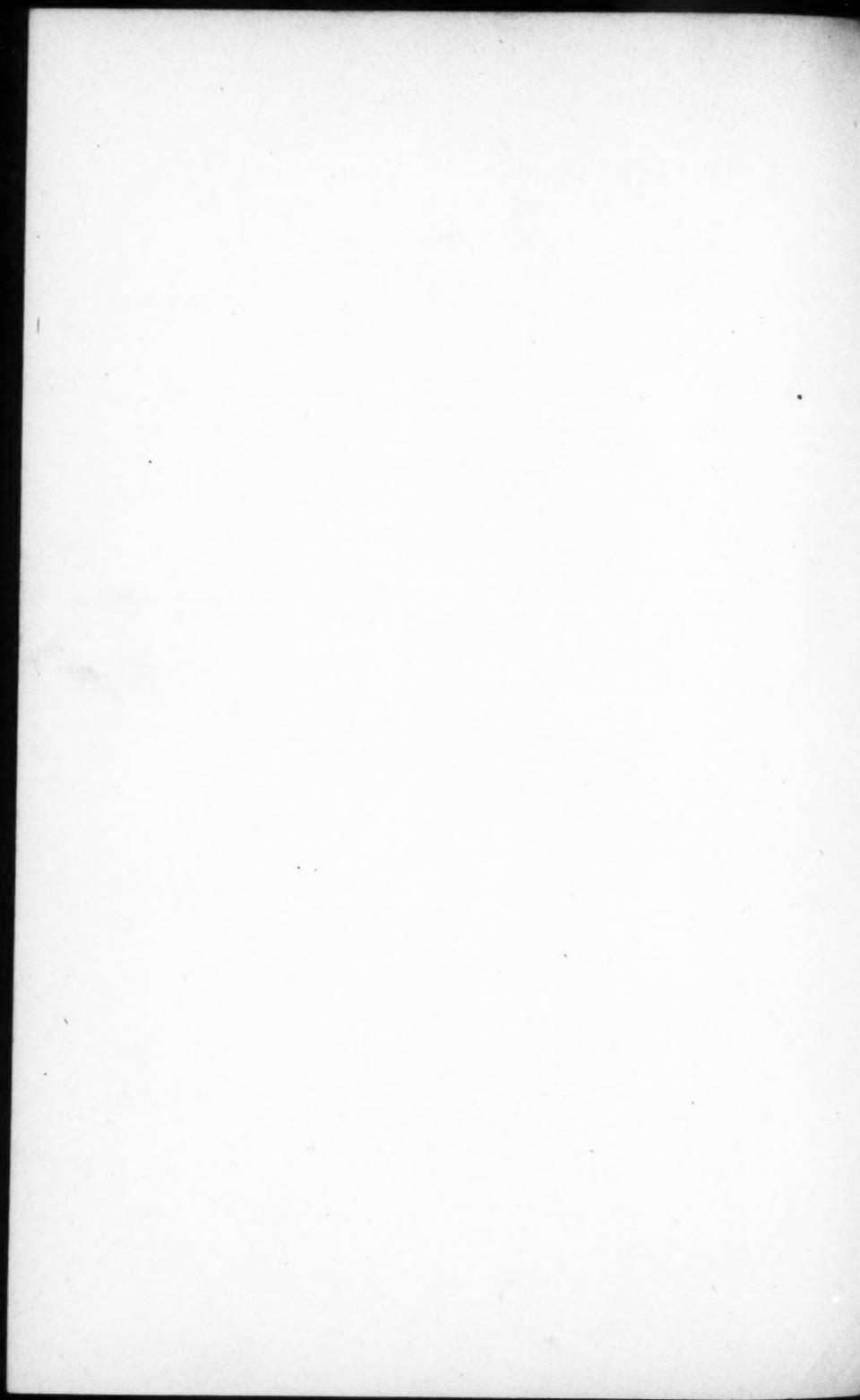
Proceedings of the American Academy of Arts and Sciences.

VOL. XLIV. No. 14. — MARCH, 1909.

CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL
LABORATORY, HARVARD UNIVERSITY.

THE PROPERTIES OF AN ALUMINIUM ANODE.

BY H. W. MORSE AND C. L. B. SHUDDMAGEN.



CONTRIBUTIONS FROM THE JEFFERSON PHYSICAL
LABORATORY, HARVARD UNIVERSITY.

THE PROPERTIES OF AN ALUMINIUM ANODE.

By H. W. MORSE AND C. L. B. SHUDDEMAGEN.

Presented by John Trowbridge, December 9, 1908. Received January 6, 1909.

I. INTRODUCTION.

MANY of the metals exhibit peculiar properties when used as anode with certain electrolytes in an electrolytic cell. Iron and chromium and, in less degree, nickel and several other elements, assume the so-called "passive state" under these conditions. Some other metals, among them aluminium, magnesium, tantalum, and niobium, show a still more striking change from their usual properties when the same conditions are imposed upon them. If the surface of metallic aluminium is kept free from the protecting film which usually covers it, it is rapidly attacked by the oxygen of the air. It is a familiar lecture experiment to carefully amalgamate a piece of clean aluminium by rubbing it with pure mercury. At the places where the mercury prevents the protecting oxide film from forming, the action of the air is so rapid that a white fibrous mass of oxide, several millimeters in thickness, grows up in a few minutes. While pure aluminium is very sensitive to an attack of reagents, it can under some circumstances act like a noble metal. As long as the film which forms on the surface retains its coherence aluminium is stable in the air, and even when it is used as anode in an electrolytic cell it may, under some circumstances, resist corrosion and solution to a surprising extent. Metals like copper and silver, which lie far down toward the negative end of the electromotive force series of metals, readily go into solution when used as anode in an electrolytic cell, but a plate of aluminium in contact with many electrolytes merely covers itself with a protecting layer and remains otherwise unattacked.

The protecting layer so formed offers a hindrance to the passage of a current through the cell as long as the aluminium plate remains the anode. If the current is reversed, the film no longer opposes the same resistance to its passage. These facts determine the use of aluminium

in the rectification of an alternating current. Below a certain critical voltage, which is a function of the electrolyte and the temperature, the film which forms on an aluminium plate is a more or less efficient valve, which permits of the passage of an electric current in one direction and not in the other. The same facts determine the application of an aluminium plate as a condenser.

II. HISTORICAL.

Wheatstone (74) appears to have been the first to notice the anomalous behavior of an aluminium anode, and he mentions it merely in connection with an investigation on the position of various metals in the voltaic series. Soon afterward Buff (10) noticed the remarkable fact that a battery of nine Bunsen cells was insufficient to cause the flow of an appreciable current through a voltaic cell in which aluminium was anode. In 1869 Tait (72), using more delicate apparatus, measured the polarization produced at anodes of various metals and found a very high polarization electromotive force to be characteristic of aluminium. During the twenty years following this date a very great number of measurements on galvanic polarization and polarization capacity of electrodes were made all over the world, and the anomalous behavior of an aluminium anode was the subject of frequent notice. The first suggestion that this property might be made use of in the rectification of an alternating current appears to have been offered by Ducretet (22), and occasional suggestions of the possibility of using aluminium plates immersed in a proper electrolyte as a substitute for a static condenser are to be found in these earlier papers. The first actual measurement of the apparent capacity of such a cell is perhaps that of Streintz (69), who showed that a formed aluminium anode can be used in this way, measuring the capacity of the plate up to 28.8 volts. He assumed, as many others have done, that an aluminium anode acts like a nearly perfect condenser, and that a short time of insulation between charge and discharge introduces no error into the measurement and may therefore be neglected. Oberbeck (52) calculates the capacity per square centimeter of anode surface, and from this value, assuming a dielectric constant, he also calculates the thickness of the active insulating film. Application of aluminium plates immersed in an electrolyte as a substitute for an ordinary condenser for practical purposes was suggested by Haagn (34) in 1897. Pollak (55) had already tested the aluminium rectifier practically, and Graetz (29), working quite independently, also showed the possibility of applying the properties of an aluminium anode in the commercial rectification of an alternating current. This was in 1897, and by far the greater part of the scien-

tific and commercial investigations on the aluminium anode which have been made since that date have had direct reference to its application as a rectifier.

III. POLARIZATION CAPACITY IN GENERAL.

It has been known for a very long time that the changes produced in an electrolytic cell by the passage of a current resulted in setting up what is called the *counter electromotive force of polarization*. It was also recognized at an early date that a corresponding *polarization capacity* was a property specific for each metal in a given solution under given conditions of current density and temperature. Kohlrausch¹ was the first to offer a formal theory in connection with measurements made on various cells with an alternating current, and he showed that an equation of form

$$iR = E \sin \omega t - L \frac{di}{dt} - p \int i dt$$

should hold, p being the counter electromotive force of polarization, which replaced the $\frac{1}{C}$ of the ordinary equation. The integrated form for the resulting wave contained a sine function and two exponentials whose value was negligible under the conditions of the experiment. If Kohlrausch's equation is true, it is evident that the current due to polarization must lead the applied electromotive force by 90° , while the lag due to inductance has the same value. He suggests the possibility of compensating the lag due to inductance by the introduction into the circuit of a polarization cell of the proper size. The current would thus be brought into phase with the applied electromotive force, and the current curve would then have the same form and position as if no inductance were present in the circuit. It has since been shown that Kohlrausch's simple theory does not hold for all the forms of galvanic polarization. It is possible to set up polarization cells in which the phase shift has any value from zero to 90° . The present theory has been given by Wien, Warburg, Elsa Neumann, and Krüger,² and the general equation for the polarization e. m. f. is

$$p = \frac{E}{C\omega} \sin \left[\omega t - \left(\frac{\pi}{2} - \theta \right) \right]$$

¹ Pogg. Ann., **148**, 43 (1872).

² Wien, Wied. Ann., **58**, 37 (1896); and Drude's Ann., **8**, 372 (1902); Warburg, Wied. Ann., **67**, 493 (1899); Neumann, Wied. Ann., **67**, 499 (1899); Krüger, Ztsch. f. Phys. Chem., **45**, 1 (1903), and Drude's Ann., **21**, 701 (1906).
VOL. XLIV. — 24

in which θ may have any value from zero to 90° . $-\left(\frac{\pi}{2} - \theta\right)$ is the lag of p behind E , and θ depends on the nature of the electrodes and the electrolyte.

This theory has been built up on the basis of Nernst's theory for the single electromotive force of an electrode in a solution containing its ion, and the theory fits the majority of cases very closely indeed. For most metals the maximum of polarization lies below three volts. This means that if we raise the electromotive force applied about the cell beyond three volts, the polarization no longer increases. This is true whether the electrode is a gaseous one, a reversible one (a metal in contact with a solution of its own ion), or any other combination of metal and electrolyte. In all of these cases there enters into the equation of the polarization electromotive force the ratio of concentrations in the ordinary Nernst form

$$E = \frac{RT}{nF} \ln \frac{C_0}{C_1}$$

It is then a familiar fact that the polarization electromotive force does not rise above three volts in any ordinary electrolytic cell. It is possible to raise the voltage of a cell having an aluminium anode at least as high as 500 volts, and it is possible to raise the voltage about cells having anodes of other metals, tantalum for example, to 1200 or even 1500 volts without reaching a point corresponding to the maximum of polarization as found for ordinary metals. If an aluminium anode has been properly "formed," that is, exposed to an electromotive force which is slowly increased step by step, the cell offers a remarkably complete barrier to the passage of a current. A small residual current flows through the cell under these circumstances, but this falls to a few milliamperes per square centimeter of electrode surface even when the applied electromotive force is measured in hundreds of volts. It seems quite evident that the process which takes place here is not polarization in the ordinary sense of the word. The substitution in the Nernst equation of the value for the "counter electromotive force" of a cell containing an aluminium anode leads to what appear to be absurd values for the ratio of the concentrations of the ion at the electrode and in the electrolyte.

IV. THEORIES OF THE ALUMINIUM ANODE.

The special characteristic of aluminium and a few other metals appears to be a film which forms on the metal when it is used as anode,

and the various theories which have been put forward to explain the behavior of these metals are all connected with the nature of this film. The theories may be summarized as follows :

1. The anode becomes covered with a *thin oxide film* during electrolysis. This oxide film may produce the effects mentioned: (a) By opposing an actual ohmic resistance to the passage of the current in one direction : (b) By acting as a dielectric pure and simple : (c) By acting as a semi-permeable membrane which prevents the passage of the anion and permits the cation to pass freely.

2. The active film is a thin *layer of oxygen gas*. This acts as a dielectric, and the entire system is a true condenser. According to this theory the visible film on the aluminium plate, whatever its chemical composition may be, plays only a secondary part in the process. It serves merely as a support for the gas layer which is produced between it and the plate.

So far in the history of the subject no crucial tests have been found which can decide definitely in favor of one theory or the other. A resistance pure and simple seems insufficient to account for the facts. The resistance in this case must be a variable quantity, decreasing as the current increases, and it must furthermore be of a different order of magnitude in two directions through the cell. Nor do we need a "transition resistance" to explain the facts. There is evidence of the most trustworthy kind that oxygen plays a considerable part in the phenomenon, but it is just as evident that it is not necessarily the only factor. The semi-permeable film theory has much to support it. Membranes have been prepared by precipitating aluminium hydroxide on the surface of a platinum plate, and even in the pores of an earthenware cup, and these membranes are capable of exhibiting all the important peculiarities of an aluminium anode formed in the usual way by electrolysis. It seems evident that neither chemical investigation alone nor the measurement of electrical properties alone can give a satisfactory answer to all the questions which arise concerning the nature of the film and its action in the cell. Chemical investigation has shown that the film consists largely of aluminium oxide or hydroxide, and that oxygen gas is also invariably present in it, and this much we may certainly take as definitely determined.

In the earlier period of research on electrolytic polarization some measurements were made with galvanometers more or less ballistic in nature. Streintz (71) called attention to the fact that the discharge from an aluminium plate used as anode consists essentially of two parts, one of which was of the nature of a condenser discharge practically complete within a fraction of a second. The other portion of

the discharge, which is superposed over the first portion, takes place more slowly and is therefore difficult to measure by ballistic methods.

When alternating currents came into common use, they were immediately applied in the study of polarization, and the great majority of the measurements which have been made in late years on aluminium anodes have been made by alternating current methods. We have thought it best to return to the older and more difficult method of the ballistic galvanometer, for previous investigations have shown that the film changes very rapidly in properties from the time a current begins to pass through it, and that every change in the electrical condition of the circuit is accompanied by a time change in the film itself. Alternating current measurements cannot give the details of this change, but only an integrated result.

V. EXPERIMENTAL RESULTS.

In beginning these measurements we had clearly in mind the difficulties mentioned by Streintz (71). The total discharge from an electrolytic cell having an aluminium anode extends over a considerable time, and it would seem, therefore, at first sight, that a ballistic method would be poorly adapted to the study of it. It was found, however, by using several ballistic galvanometers of different period, that the error due to the slow residual charge could be neglected; by using plates of considerable surface and low resistance ballistic galvanometers of rather long period, it was practically eliminated.

Anodes were formed either from a storage battery or from a dynamo current, and after formation they were charged from a storage battery of small cells capable of giving over 500 volts. The time measurements were made by the apparatus shown in Figure 1. This is merely a simple machine which allows a heavy weight to fall, contacts being made and broken by the weight as it passes. The switches to be opened or closed

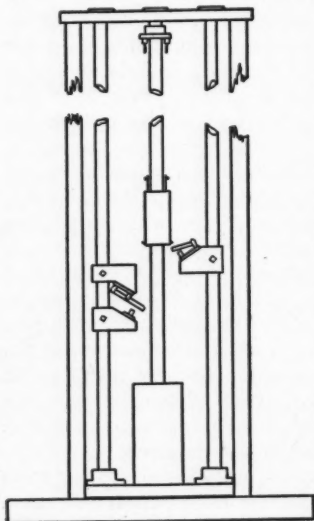


FIGURE 1.

Apparatus for charging and discharging condensers.

are clamped to the side rods and the times are calculated from the velocities of the falling weight as it meets the switches. The maximum time of charge, discharge, or insulation which can be obtained with this apparatus is about 0.6 seconds. Longer times than this are measured with a stop watch. The minimum time is limited only by the delicacy of the contacts used, as they must always be made strong enough to withstand the heavy blow of the falling weight. The minimum time in

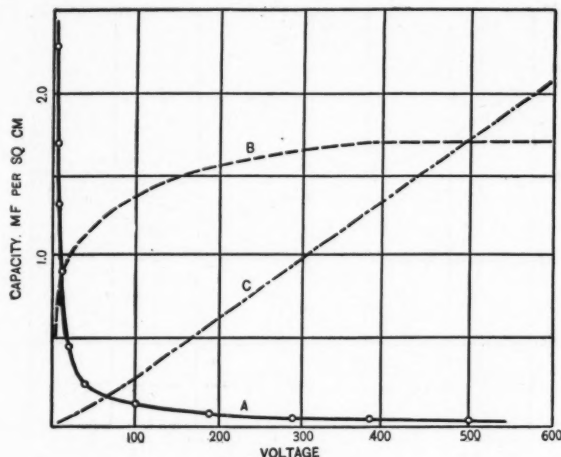


FIGURE 2.

- A. Capacity of an aluminium condenser at various formation voltages.
 - B. Quantity = $C \times V$ from curve A.
 - C. Energy = $C \times V^2$ from curve A.
- Long charge. Long discharge. Insulation time, 0.002 seconds.

most of our experiments is of the order of 0.001 seconds, and this can be measured with considerable accuracy. Three ballistic galvanometers were used in this work. Where a long series of measurements was to be made, involving a large range of capacities, the first readings at higher voltages were made on the least sensitive galvanometer, and as the voltage was decreased until the throw of this galvanometer was no longer sufficient to give the necessary accuracy, connections were thrown over to the second and more sensitive galvanometer and readings continued with its aid. The periods of the galvanometers were 1, 4, and 9 seconds respectively. It has already been mentioned that the discharge

from an aluminium film may be considered to consist of two portions, one of which takes place so slowly that part of it passes through the circuit even after the slowest of our galvanometers begins its swing. The results of careful preliminary tests made it probable that this error would be negligible in our measurements, and the experimental results all confirm this assumption. The galvanometers were calibrated against standard mica condensers charged from a storage battery, and the

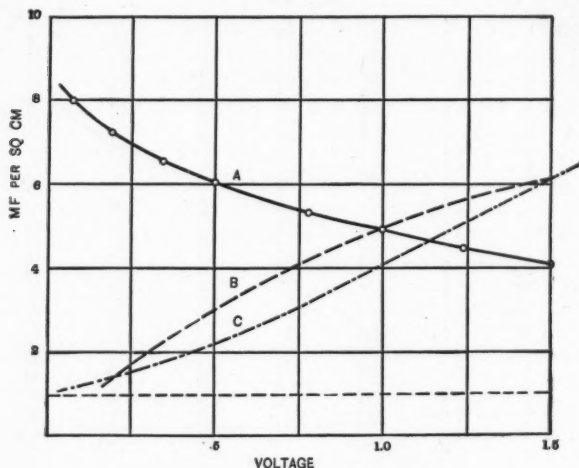


FIGURE 3.

Capacity (A), Quantity (B), and Energy (C) curves for low formation voltages. From tables of Scott (64) and our own measurements. Long charge. Long discharge. Insulation time, 0.002 seconds.

calibration was repeated several times during the progress of the measurements.

1. *Apparent Capacity and Forming Voltage.* — In Figure 2 the apparent capacity in microfarads per square centimeter of anode surface is plotted in curve A against the forming voltage applied to the cell, the charging voltage being in this case the same as the forming voltage. The following factors are constant throughout this curve: charging time, 1 minute; insulation time, 0.002 sec.; discharge time, complete. The cell was left short-circuited through the galvanometer. It is evident that the curve approaches an hyperbola in its general course, and it has been assumed by Gordon (27), Corbino and Maresca (17), Schultze

(58), and others, that it is an equilateral hyperbola, and that therefore the product of apparent capacity and forming voltage is a constant. A careful examination of the data of the curve shows that this is by no means the case. The curve marked B gives the values for the product capacity \times forming voltage (in this case applied voltage also), and this should be of course a straight line parallel to the X axis if the product is to be constant. The third curve, C, of Figure 2 gives the value for the

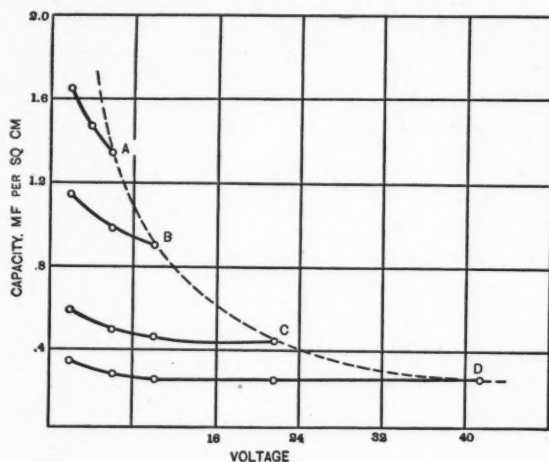


FIGURE 4.

Capacity at less than forming voltage. For the lower range of voltages.

Same times of charge, discharge, and insulation as in Figures 2 and 3.

Curve A.	Formed at 6 volts.	Measured at 6, 4, and 2 volts.
B.	" 10 "	" 10, 6, and 2 volts.
C.	" 21 "	" 21, 10, 6, and 2 volts.
D.	" 41.6 "	" 41.6, 21, 10, 6, and 2 volts.

energy per square centimeter stored in an aluminium anode when various voltages are applied to it, and this is very nearly a straight line with only a slight curvature for voltages lower than 100. Figure 3 indicates the characteristics of these curves at very low voltages. The data for this particular curve were taken from the measurements of Scott (64), but it is in close agreement with our own results in the same voltage range. It is quite evident that the product of capacity and voltage is not constant, and for these conditions the curvature in the energy curve is also more evident. The values obtained for the capacity of an alu-

minium anode at voltages below two volts are of the same order as polarization capacities found for other metals in electrolytic cells. They are, however, smaller than most of these, the maximum value observed for aluminium being about 8 microfarads per square centimeter, while other metals often show several times this capacity.

An examination of the various measurements we have made on different aluminium anodes shows a remarkable agreement in properties.

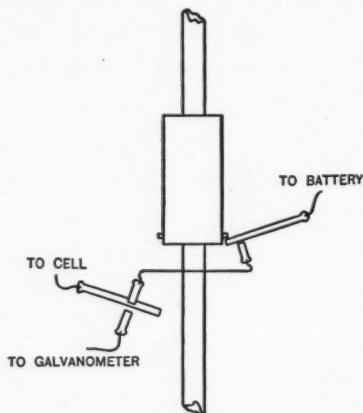


FIGURE 5.

Arrangement of switches for varying short charge. Short insulation and long discharge.

ily of curves gives an indication of the complexity of the active film. The same times of charge, discharge, and insulation as were used in the previous measurements were maintained in these.

The plate was first formed at 6 volts, and measurements were taken at 6, 4, and 2 volts. The results are plotted in the upper curve. Formation was then continued, and completed at 10 volts, and the results of measurements at 10, 6, and 2 volts are given in the second curve. The other curves give similar results up to a forming voltage of 41.6, measurements being made in each case at the forming voltage and then at several lower voltages. It will be seen from this figure that whatever the nature of the film may be, and whatever the mechanism by which it acts, the capacity is greater at voltages lower than the

It is possible to reproduce a capacity with different samples of aluminium, with electrodes of different area, but which have been formed at the same voltage, with an accuracy apparently as great as 2 per cent. Other factors, such as temperature, electrolyte, time of charge, discharge, and insulation, etc., must of course be kept constant, but when these conditions are met, and notwithstanding the complex nature of the film involved, the capacity is a very accurate function of the voltage at which the plate has been formed.

2. *Capacity below Forming Voltage.*—Figure 4 gives the results of a set of measurements of capacity at voltages less than forming voltage, and this fam-

forming voltage through the range of voltages indicated. The dotted curve is a portion of the capacity curve of Figure 2.

Capacities at various voltages below forming voltage have been measured by other investigators. Corbino and Maresca (17) give several tables of data on the point, but all of their results are in contradiction to the ones we have obtained. They find that in every case capacity

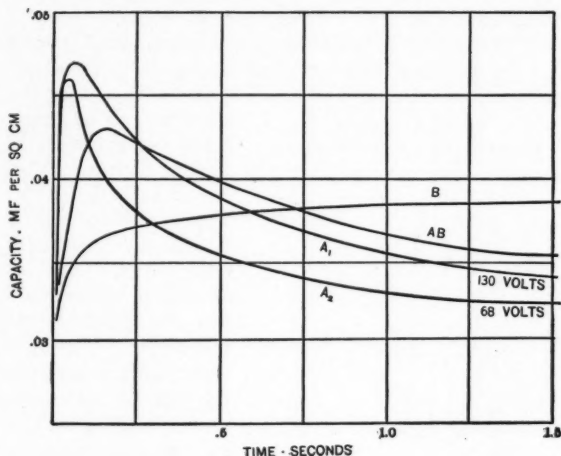


FIGURE 6.

Charging time curves. A, for very fully formed plate. B, ordinary curve for average plate. AB, intermediate condition. Insulation time, 0.002 seconds. Full discharge.

Curve A ₁ .		Formed at 340 volts.		Measured at 130 volts.	
A ₂	"	340	"	"	68 "
B.	"	340	"	"	130 "
AB.	"	340	"	"	130 "

at voltages below forming voltage is lower than at forming voltage itself. Figure 4 expresses the average of a great many observations, and further confirmation of the correctness of these results will be found in Figures 11 and 12, which give data on apparent capacity below forming voltage after the cell has been left on open circuit for varying lengths of time. The matter is a complex one, and can only be considered as a whole after the other factors involved have been taken up individually. Reference to Figure 17 shows that the capacity is not under all circum-

stances higher below forming voltage than at this point. It may in fact be either lower or higher than the capacity at forming voltage. It will be seen from Figure 17 that if one is working with long charge, short insulation time, and long discharge, the capacity is represented by the curve marked A. Under these conditions the apparent capacity of the plate is greater at low voltages and less at intermediate voltages than it is at the forming voltage itself. This matter will be taken up more fully after the other factors have been discussed.

3. *Short Charge.*—Figure 5 shows the arrangement of apparatus for measuring the apparent capacity of an aluminium anode after it has

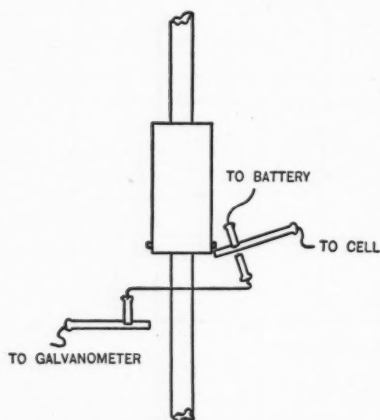


FIGURE 7.

Arrangement of switches for long charge. Short insulation and varying short discharge times.

been charged for variable short periods of time. The falling weight closes the upper switch, thus completing the circuit from the storage battery through the cell. Falling further, the weight opens this same circuit, and immediately afterwards closes the circuit from the cell through the galvanometer. The insulation time, which is determined by the distance between the two lower switches, is kept constant at 0.001 second, and the variable charging time is fixed by moving the upper switch up or down on the side rod. Reference to Figure 1 will make this clear.

The results of measurements made in this way show that factors still undetermined

play an important rôle. The previous history of the plate becomes of great importance, and wholly different results are obtained from plates which have been formed slowly and carefully and from those which have been hastily formed, or which have been exposed directly to the voltage of the experiment without previous formation.

Figure 6 gives a set of characteristic curves of apparent capacity (ordinates) for various short charging times (abscissas). The two curves marked A_1 and A_2 are characteristic of a plate which has been very carefully and fully formed. This plate was formed at 340 volts, and

the two A curves were taken at 130 volts and 68 volts respectively. Under these conditions the shape of the curve is a remarkable one. It evidently takes time for the film to attain its optimum condition, and this was to be expected. But the apparent capacity begins to decrease again after a short time of charge, and this result was an unexpected one.

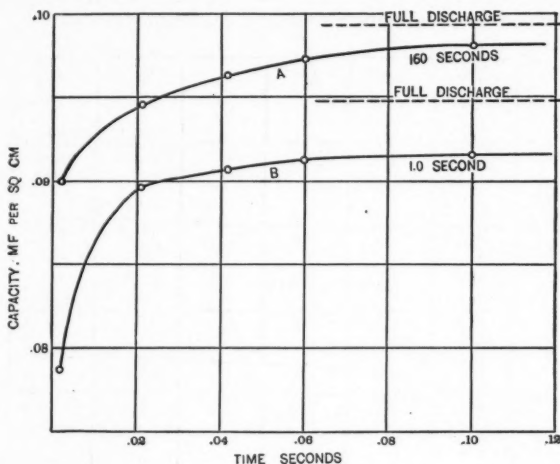


FIGURE 8.

Discharge curves at lower voltages for a very fully formed plate. Plate formed at 140 volts, charged at 67 volts.

We have found similar results for several plates, and there is no reason to doubt that such curves correspond to real physical conditions.

The curve marked B may be taken as representative of another series of measurements on other plates, and this curve we have also found repeatedly. It corresponds to a difference in the previous history of the plate under examination and apparently belongs to incomplete or rapid formation. While the apparent capacity of an "A" plate has its maximum value for a charging time of 0.03 to 0.1 second, that of a "B" plate increases with charging time without passing through a maximum, becoming asymptotic within a few seconds to the value found for a very long time of charge.

We have also found occasionally curves similar to that marked AB. This appears to correspond to a condition of formation intermediate between the two others.

There is evidently a close connection between the data of Figure 6 and the results to be expected from a study of an aluminium condenser under the action of an alternating current. As will be seen from succeeding figures, the relation will be a complicated one, because of the influence of insulation time and discharge time.

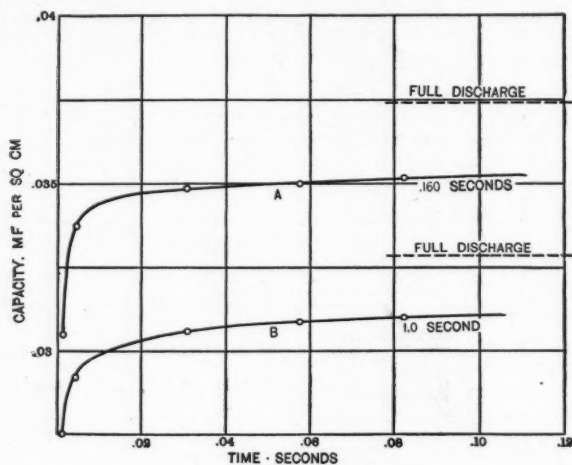


FIGURE 9.

Discharge curves at higher voltages for fully formed plate, as in Figure 8. Plate formed at 340, charged at 195 volts.

4. *Short Discharge.* — Figure 7 shows the arrangement of apparatus for measuring the apparent capacity during a short time of discharge. The insulation time is kept constant at 0.001 second. The charging time, which determines a difference in capacity, as shown by the previous figure, has been given two different values. As shown in the figure, the apparatus is arranged for long charging times, the upper switch being closed and thus connecting the cell with the charging battery. The falling weight opens the charging circuit and closes the discharge circuit after the period of insulation; the weight falling further opens the galvanometer circuit when it strikes the lower switch. The apparatus for measuring the capacity for short

discharge time after a short charging time is different only in the fact that the falling weight closes the charging circuit as it descends, the remainder of the switches being thrown as already indicated.

The data for Figures 8 and 9 was taken on the same plates as were used in obtaining the A curves of Figure 6, and they show again the fact to which attention was called at that point: the apparent capacity is, for all times of discharge, greater for a short time of charge than for a longer one. The dotted lines indicate full discharge. The cell is left short-circuited through the galvanometer to obtain this value.

For a plate similar to that which gave the B curve of Figure 6 the A and B curves of Figures 8 and 9 will merely exchange positions. In this case a longer charge corresponds to a greater apparent capacity for all times of discharge.

Plates having charge-time characteristics like those shown in the AB curve of Figure 6 will show a corresponding set of discharge curves.

The plate of Figure 8 was formed at 140 volts, and both the curves were taken with an applied voltage of 67 volts. The plate of Figure 9 was formed at 340 volts, and the working voltage was 195.

5. *Insulation Times.* — Figure 10 shows the arrangement of switches for the third of the time factors, variable periods of insulation. As the figure is drawn arrangement is made for long charging times, the upper switch being closed, so that the current passes from the charging battery through the condenser until it is opened by the falling weight. This opens all the circuits, and the cell is then closed through the galvanometer after an insulating time depending upon the distance between the two lower switches. Measurements with short charging times were also made, and for this purpose a third switch is introduced higher up, which is closed first of all by the falling weight. Figures 11 and 12 give the results of these measurements for a con-

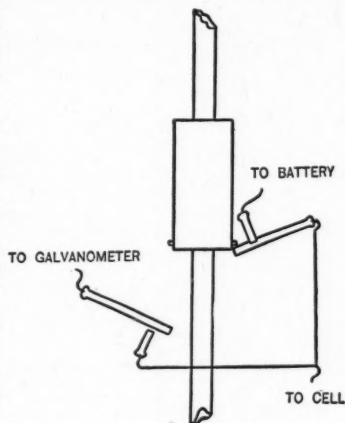


FIGURE 10.

Arrangement of switches for long charge, long discharge, and varying short insulation times.

stant long charging time (1 minute), complete discharge, and a variable time of insulation. The curves for short charging times are similar in form, but lie a little above or below the curves given. These curves show very clearly the point already mentioned, that such a condenser can under certain conditions act more perfectly at voltages below the voltage of formation.

It is also of interest to know the shape of the leak-curves at the forming voltage itself. Data on this factor is given in Figure 13 for

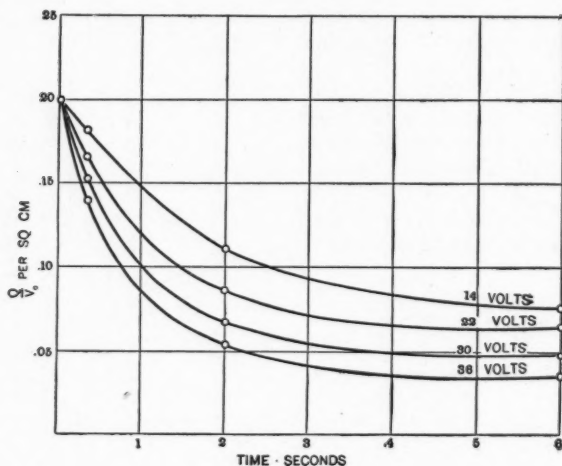


FIGURE 11.

Capacity vs. insulation time. Plate formed at 36 volts. Curves for 36, 30, 22, and 14 volts. Long charge. Long discharge.

plates formed at 36, 80, 140, and 300 volts. They offer one means of examining the change which takes place in the active film during insulation, but they are complicated by all the other factors involved, and it seems probable that the study of such curves can only lead to a definite solution of the problem when they are examined in connection with the other variables. They do not appear to follow any simple exponential formula.

It should be noted that in these last cases we have not measured a true capacity, but values of Q/V after various times of insulation. The "condenser" is so leaky that even during a very short time of

insulation it loses a considerable portion of its charge. The actual capacity could only be found by a method which permitted of the measurement of the voltage about the cell immediately before the discharge through the galvanometer began. It would therefore be better to consider the ordinates in some of our curves as Q/V , rather than *apparent capacity*. This applies to Figures 11, 12, 13, 14, and 15.

In any case our condenser is a very leaky one indeed as compared

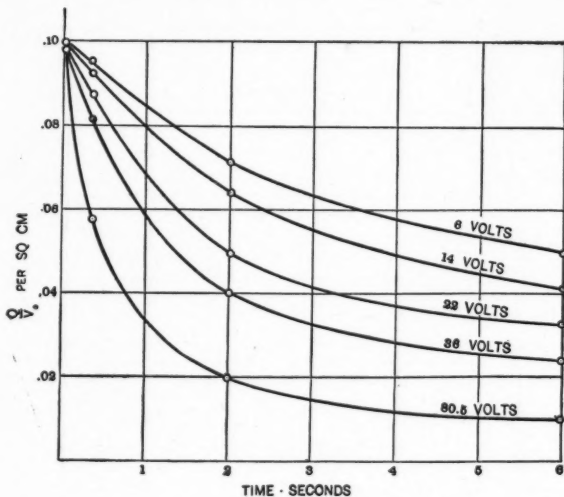


FIGURE 12.

Capacity vs. insulation time. Plate formed at 80.5 volts. Curves for 80.5, 36.5, 22, 14, and 6 volts. Long charge. Long discharge.

with a static condenser of even the poorest construction, but the difference in the leakage losses at the forming voltage and at a much lower voltage is very great for considerable insulation times. As the insulation time is made shorter and shorter, the difference in the capacity at various voltages becomes less and less, and for very short insulation times the capacity is practically the same for all voltages below the forming voltage. These differences are clearly shown in Figures 14 and 15. In these two figures capacity is plotted against applied voltage, and the curves represent various insulation times. It will be seen that the curve for short insulation time indicates a prac-

tically constant capacity at all voltages below the forming voltage. The curves of Figures 11 and 12 may be regarded as tests showing the approximation to true condenser action which is attained with aluminum electrodes. For an ordinary mica or paper condenser the rate of leak during insulation is of such a form that the charge remaining in the condenser is

$$Q = Q_0 e^{-\frac{t}{CR}}.$$

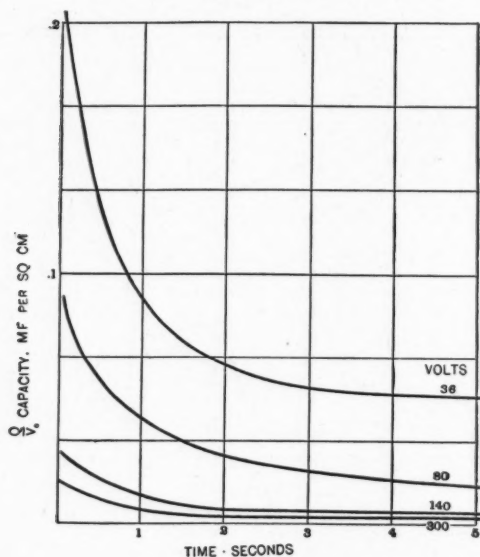


FIGURE 13.

Capacity vs. insulation time at various forming voltages. Long charge. Long discharge.

If the logarithm of the remaining charge is plotted against insulation time, the resulting curve is a straight line. Figure 16 shows the curves obtained by plotting the data of Figure 12 in this way. It is quite evident from these curves and from the results of time measurement on charge and discharge that we are not dealing with a true condenser. It will be noticed that at voltages far below that of formation the curve of leak follows the logarithmic formula quite closely. In all

the curves we have plotted there is, however, a perfectly definite curvature near the beginning of the curve. This point will probably be found of importance in the study of the *efficiency* of aluminium condensers. It is evident from the data at hand that the separation of the effect of capacity from the effect of resistance can probably not be carried out by ballistic measurements on these films. One method which would probably be successful in the separation of these two

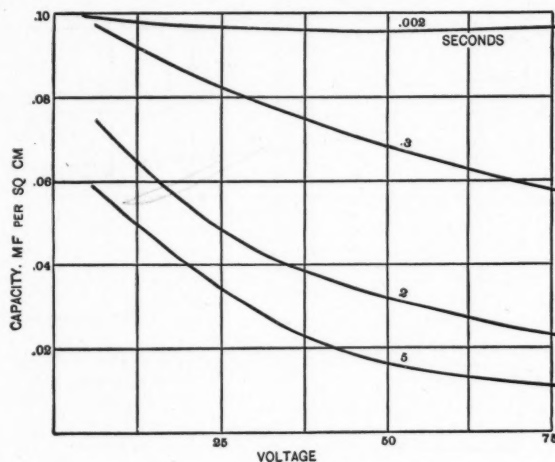


FIGURE 14.

Capacity vs. voltage (below forming voltage) for various insulation times. Curves for times .002 seconds, 0.3 seconds, 2.0 seconds, and 5.0 seconds. Lower range of voltages.

factors would involve the study of resonance conditions in circuits containing capacity, resistance, and inductance.

6. *Variations in Both Charging Time and Insulation Time.* — We have collected a large mass of data on individual cases in which both charging time and insulation time are varied. This data does not appear at present to be of sufficient value to warrant publication as a whole. The general course of the curves is shown in Figure 17, and the times are indicated below that figure. Several of the facts already mentioned are evident from this figure. The variation in capacity below forming voltage is clearly seen, and the change which takes place as the insulation time is increased is also plain. Similar curves

were found for all voltages, and this set of curves may therefore be considered characteristic.

7. *Three Dimensional Diagrams.*—In the five succeeding figures some of the factors so far studied are plotted in groups of three. It would require a great deal of space and many figures to represent all our data in the usual way, and the conclusions which can be drawn are so far not of a sufficiently quantitative nature to demand great accu-

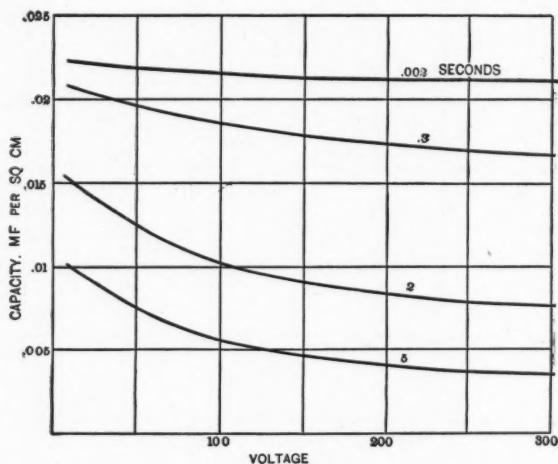


FIGURE 15.

Same as Figure 14 for higher range of voltages.

acy in the presentation of data. It is easier to grasp the meaning of the data when it is arranged as compactly as possible. We have therefore made use of curves in place of tables of data, and it is hoped that the three-dimensional diagrams will take the place of the large number of curves which they represent.

Figure 18 is a composite figure in which apparent capacity, charging time, and forming voltage are plotted together, the charge being given at the forming voltage.

The diagrams represent the results which we obtained with an aluminium anode which was rather hastily formed for part of the measurements and very carefully and slowly formed later in the series. The low voltage curves therefore show no maximum of charge for a short

charging time, while the curves taken at higher voltages after very slow formation show such maxima. The dotted curves are the A curves of Figure 2, and it is evident that these curves may not be the same over the whole sheet which they enclose. This variation, if any exists, we have not yet sifted out from the mass of experimental data.

In Figure 19 apparent capacity, discharge time, and forming voltage are plotted together. At low voltages the discharge curve runs up

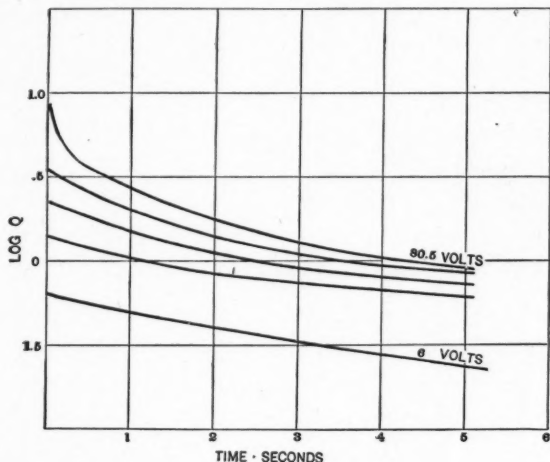


FIGURE 16.

Test of character of leak and of formula $Q = Q_0 e^{-\frac{t}{CR}}$. Log Q vs. insulation time.

rather slowly. As the voltage is increased the curve rises more quickly and the turn toward the asymptote (full discharge) is sharper. Here again the dotted lines are A curves of Figure 2, as in Figure 18, and here also it seems very probable that there is variation in the shape of these curves across the sheet which they enclose.

In Figure 20 apparent capacity, insulation time, and voltage (below forming voltage) are expressed in one diagram. The full curves are a family similar to that in Figures 11 and 12, and the dotted curves are those of Figures 14 and 15, each a line of constant insulation time. It is probable that these curves turn upward rather sharply at very low voltages, but we have only a few scattered observations on this point.

Figure 21 has apparent capacity, insulation time, and *forming voltage* as its co-ordinates, the charging voltage being that of formation. The heavy curves are similar to those of Figure 13, and the dotted lines are now A curves of Figure 2, since capacity is measured at the voltage of formation.

Finally, in Figure 22 we have plotted the apparent charge of a plate formed at various voltages, and measured at various voltages below

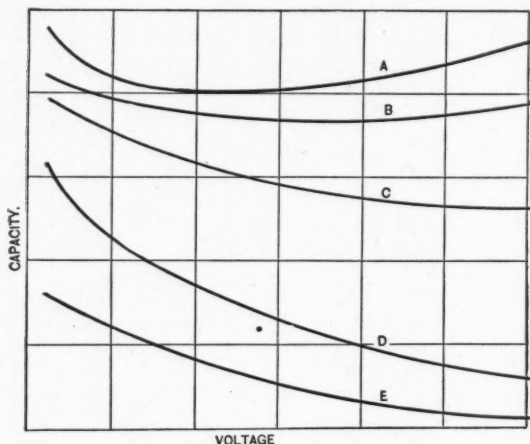


FIGURE 17.

Capacity vs. voltage (below formation voltage) for various time combinations.

Curve A.	Charging time, long.	Insulation time, .002 sec.	Disch. time, long.
B.	" 0.5 sec.	" " .002 sec.	" " "
C.	" 0.16 sec.	" " 3.00 sec.	" " "
D.	" long.	" " 2.0 sec.	" " "
E.	" long.	" " 5.0 sec.	" " "

that of formation. The full curves are somewhat like those of Figure 4 and the A and B curves of Figure 17. This means that the plate (average formation assumed) is being given a fairly long charge and a short period of insulation. The curves, therefore, will in general rise at rather low working voltage, and the sheet will be somewhat hollow. The projections of these curves are indicated on the plane at the left. These curves have not the same numerical value as those of Figures 4 and 17, but they are somewhat similar in shape, the ordinates being

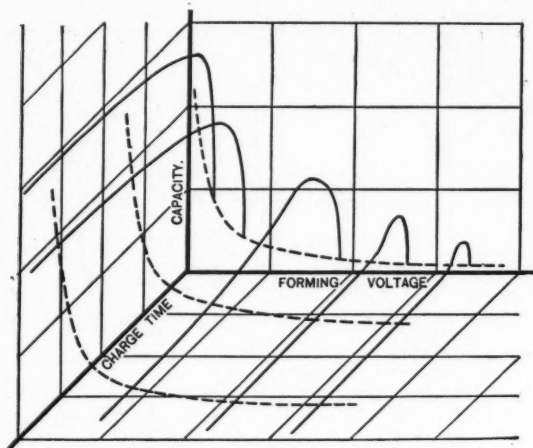


FIGURE 18.

Capacity vs. charging time at various forming voltages. The dotted curves correspond to the A curve of Figure 2.

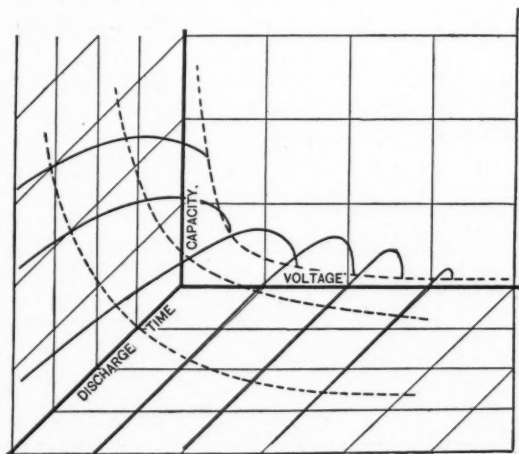


FIGURE 19.

Capacity vs. discharge time at various forming voltages. The dotted lines correspond to the A curve of Figure 2.

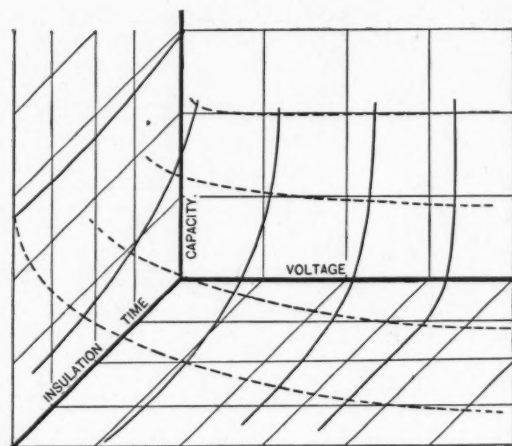


FIGURE 20.

Capacity *vs.* insulation time at various voltages below forming voltage. The dotted lines correspond to the curves of Figures 14 and 15.

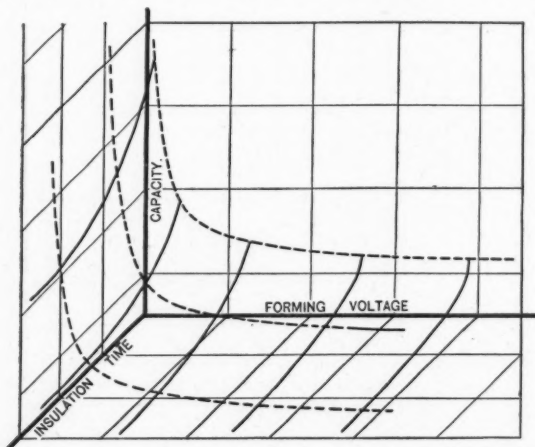


FIGURE 21.

Capacity *vs.* insulation time at various forming voltages. The dotted lines correspond to the A curve of Figure 2.

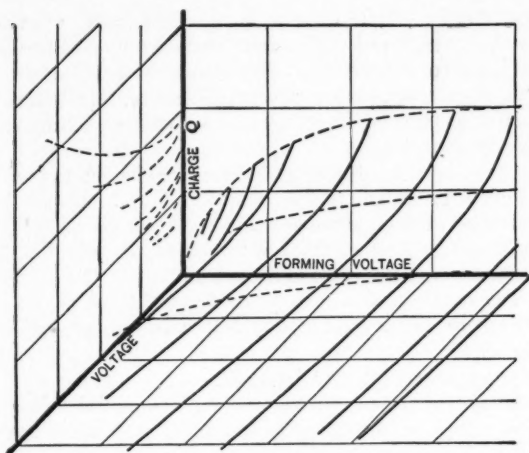


FIGURE 22.

$K = CV$ vs. voltages for plates formed at various voltages. The curves parallel to the plane of the paper correspond to the B curve of Figure 2. The dotted lines on the YZ plane are traces of the main curves (full line) on this plane.

obtained by multiplying by a constant (the forming voltage). The dotted lines will then be B curves of Figure 2 as far as they go. They are of course limited by the fact that the plate is only charged at voltages less than the formation voltage.

VI. THE FACTORS WHICH DETERMINE CAPACITY.

Summary. — It would appear that the following factors all enter into what we have been calling the *apparent capacity* of an aluminium anode :

1. Formation voltage.
2. Mode of formation (time, voltage-steps, etc.).
3. Applied voltage.
4. Time of charge.
5. Time of insulation.
6. Time of discharge.
7. The electrolyte.
8. Temperature.
9. Electrical constants of the circuit outside the cell.

Some of these factors appear to have a more definite influence, or rather a less complicated influence, than others. Temperature, for example, must be considered a *more general* factor than the others. They are, however, apparently all independent variables within certain limits, and a complete expression for the action of an aluminium anode must include all of them.

It may be of interest to attempt to segregate the effects produced by variation of these factors.

1. Formation voltage may determine —
 - (a) Thickness of an oxide or hydroxide film.
 - (b) Density and thickness of a gas film.
 - (c) The perfection of a semi-permeable membrane.
2. Time of formation (and history of formation in general).
Same as 1.
3. The applied voltage may determine —
 - (1 (a) should remain constant for various applied voltages below the voltage of formation unless solution by the electrolyte or other disintegrating action takes place)
 - (a) Thickness and density of a gas film.
 - (b) Ionic concentration within the active layer of the film.
4. Time of charge (complete formation assumed) may determine —
 - (a) The thickness (distributed) of an insulating or other active film.
 - (b) The ionic concentration within the active layer of the film.
5. Insulation time may determine the rate of return to the uncharged condition —
 - (a) By disintegration of an insulating solid film.
 - (b) By gas diffusion.
 - (c) By ionic diffusion.
6. Time of discharge may determine —
Factors similar to those in 5, but under conditions varying with the electrical constants of the discharge circuit.
7. The electrolyte may determine the entire activity or non-activity of the anode —
 - (a) By the ions it furnishes, which may or may not be able to pass the film it forms (semi-permeable film theory).
 - (b) By its solvent action on the film.
8. Temperature affects all the above.
9. Electrical constants of the circuit can affect 4 and 6 especially.

All of the effects enumerated are quite open to study, and some of them have already been investigated. The authors hope to offer further data on some of these variables in the near future.

It is evident from this summary that alternating current methods of measurement will give much simpler and in some respects more useful results than the ballistic method. If a definite wave-form and a definite frequency are available, we have at once disposed of charging time, insulation time, discharge time, and the constants of the circuit. Making these factors constant is a very great simplification, and the other factors can be approached much more easily than by any ballistic method. But the factors mentioned are of scientific interest, and accurate study of their variations leads to analytical results which could hardly be obtained by the aid of alternating current measurements.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY.

December 23, 1908.

LITERATURE.

1. **Askenasy.**
Ztsch. f. Elektrochem., **4**, 70 (1897). — Discussion at Bunsen Society meeting.
2. **Bartorelli.**
N. Cimento, (5), **1**, 112 (1901). — General study of aluminium electrodes.
3. **Bartorelli.**
Phys. Ztsch., **2**, 469 (1901). — Aluminium kathode especially.
4. **Beetz.**
Pogg. Ann., **127**, 45. — Polarization in general.
5. **Beetz.**
Pogg. Ann., **156**, 464. — Polarization at aluminium plate.
6. **Beetz.**
Wied. Ann., **2**, 94. — Analyses of electrode, etc.
7. **Berti.**
L'Elettricità, **11**, 101 (1902).
8. **Blondin.**
L'Eclair, Electr., **18**, 117 (1901). — Report on Pollak's rectifier.
9. **Bottome.**
Electr. Engineer, Mar. 11, 1891. — Suggests application as rectifier.
10. **Buff.**
Lieb. Ann., **102**, 269 (1857). — Polarization at aluminium anode.
11. **Burgess and Hambuechem.**
Trans. Am. Electrochem. Soc., **1**, 147. — Ohmic resistance theory.

12. **Campetti.**
Atti di Torino, **34**, 90 (1899). — Aluminium rectifier.
13. **Campetti.**
Atti di Torino, **36**, 427 (1901). — Magnesium rectifier, etc.
14. **Charters.**
Journ. Phys. Chem., **9**, 110 (1905). — General. Aluminium rectifier.
15. **Cook.**
Phys. Rev., **20**, 312 (1905). — Counter e. m. f. theory.
16. **Cook.**
Phys. Rev., **18**, 23 (1904). — Preliminary to previous paper.
17. **Corbino and Maresca.**
N. Cimento, **12**, 5 (1906). — General study of aluminium anode.
18. **Corbino.**
N. Cimento, **12**, 113 (1906). — Optical investigation of film thickness.
19. **Dina.**
Rend. Ist. Lomb., (1898), 31. — Aluminium anode.
20. **Ditte.**
Comptes rendus, **127**, 919 (1893). — Nature of the film.
21. **Dongier.**
Journ. de Phys., (4), **2**, 507 (1903). — Report and summary on rectifiers.
22. **Ducretet.**
Journ. de Phys., (1), **4**, 84 (1875). — Suggests rectification.
23. **Ducretet.**
Comptes rendus, **80**, 280. — Same as above.
24. **Fischer.**
Ztsch. f. Elektrochem., **9**, 507 (1903). — Preliminary to following papers.
25. **Fischer.**
Ztsch. f. Phys. Chem., **48**, 177 (1904). — Transition resistance.
26. **Fischer.**
Ztsch. f. Elektrochem., **10**, 869 (1904). — As above. No polarization more than 3 volts.
27. **Gordon.**
Phys. Rev., **24**, 60 (1907). — General paper.
28. **Gordon.**
Phys. Rev., **20**, 128 (1905). — Address at Phys. Soc. meeting.
29. **Graetz.**
Ztsch. f. Elektrochem., **4**, 67 (1897). — Paper read before Bunsen Society.

30. **Graetz.**
Wied. Ann., **62**, 323 (1897). — Aluminium rectifier.
31. **Graetz.**
L'Eclair, Electr., **14**, 289 (1897). — Efficiency, etc., of rectifier.
32. **Grisson.**
Elektrotech. Ztsch., **24**, 432 (1903). — New form for aluminium rectifier.
33. **Guthe.**
Phys. Rev., **15**, 327 (1903). — Ionic concentration theory.
34. **Haagn.**
Ztsch. f. Phys. Chem., **23**, 119 (1897). — Describes aluminium condenser.
35. **Haagn.**
Ztsch. f. Elektrochem., **3**, 470 (1896). — Aluminium anode.
36. **Hopkinson, Wilson, and Lydall.**
Proc. Roy. Soc., **54**, 407. — Application of electrolytic condensers.
37. **Isenburg.**
Ztsch. f. Elektrotech., **9**, 278 (1903). — Counter e. m. f. and dielectric insulating film.
38. **Jacobs.**
Electrolytische Gleichrichter. (Book.) Sammlung Elektrotechnischer Vorträge, No. 9.
39. **Laurie.**
Phil. Mag., (5), **22**, 213 (1886). — Nature of film.
40. **Lecher.**
Wien. Akad. Ber., **107**, 2a, 739 (1898). — Aluminium anode in alum solution.
41. **Liebenow.**
Ztsch. f. Elektrochem., **10**, 944 (1904). — Note on aluminium condensers in series and parallel.
42. **Maresca.**
N. Cimento, **12**, 155 (1906). — Magnesium anode.
43. **Mitkiewicz.**
Phys. Ztsch., **2**, 747 (1901). — Rectifier in three-phase work, etc.
44. **Mott.**
Electrochem. Industry, **2**, 268 (1904).
45. **Mott.**
Electrochem. Ind., **2**, 352 (1904). — Thickness and nature of film.
46. **Naccari.**
Atti di Torino, **36**, 790 (1901). — Polarization on aluminium anode.
47. **Neyreneuf.**
Journ. de Phys., (2), **7**, 250 (1888). — Suggests rectification.

48. **Nodon.**
Comptes rendus, **136**, 445 (1903). — Aluminium condenser.
49. **Nodon.**
Electrician, **53**, 1037 (1904). — Electrolytes, etc.
50. **Norden.**
Ztsch. f. Elektrochem., **6**, 159 (1899); and **6**, 188. — Chemical analyses and theory.
51. **Norden.**
Electrician, **48**, 187 (1901). — Theory.
52. **Oberbeck.**
Wied. Ann., **19**, 625 (1883). — Capacity and film thickness.
53. **Peters und Lange.**
Elektrotech. Ztsch., **26**, 751 (1905). — Effect of anion.
54. **Pollack.**
Comptes rendus, **124**, 1443 (1897). — Descriptive. Efficiencies, etc.
55. **Pollack.**
Ztsch. f. Elektrochem., **4**, 70 (1897). — Discussion at Bunsen Soc. meeting.
56. **Roloff und Siede.**
Ztsch. f. Elektrochem., **12**, 670 (1906). — Rectifier.
57. **Ruban.**
Journ. Russ. Phys.-Chem. Soc., **39**, 116 (1907). — Precipitation films, semi-permeable.
58. **Schultze.**
Drude's Ann., **21**, 929 (1906). — Electrolytes, gas-film theory.
59. **Schultze.**
Drude's Ann., **22**, 543 (1907). — Electrostatic theory.
60. **Schultze.**
Drude's Ann., **23**, 226 (1907). — Tantalum electrodes.
61. **Schultze.**
Drude's Ann., **24**, 43 (1907). — Magnesium, antimony, and bismuth electrodes.
62. **Schultze.**
Drude's Ann., **25**, 775 (1908). — Niobium electrodes.
63. **Schultze.**
Ztsch. f. Elektrochem., June 19, 1908. — Rectifier, with oscillograms, etc.
64. **Scott.**
Wied. Ann., **67**, 388 (1899). — Capacity at low voltages.
65. **Sebor und Simek.**
Ztsch. f. Elektrochem., **13**, 113 (1907). — Electrolytes.

66. **Siemens und Halske.**
German Patent, 150,883-21, g. — Tantalum, niobium, and vanadium in rectifiers.
67. **Straneo.**
L'Elettricità, **10**, 228 (1901). — Energy losses near plates and in electrolyte.
68. **Strasser.**
Elektrotech. Ztsch., **20**, 498 (1899). — Aluminium condensers in series and parallel.
69. **Streintz.**
Wied. Ann., **17**, 850 (1882). — Condenser. Capacity to 28.8 volts.
70. **Streintz.**
Wied. Ann., **32**, 116 (1887). — Polarization. Aluminium and other metals.
71. **Streintz.**
Wied. Ann., **34**, 751 (1888). — Dielectric film.
72. **Tait.**
Phil. Mag., (4), **38**, 243 (1869). — Polarization of aluminium at various voltages.
73. **Taylor and Inglis.**
Phil. Mag., (6), **5**, 301 (1903). — Semi-permeable film theory.
74. **Wheatstone.**
Phil. Mag., (4), **10**, 143 (1854). — Position of aluminium in voltaic series.
75. **Wilson.**
Proc. Roy. Soc., **63**, 329 (1898). — Alternating current measurements.
76. **Wilson.**
Electrical Rev., 1898, 371. — As above. Rectifier.
77. **Wipperman.**
Wien. Akad. Ber., **107**, 2a, 839 (1898). — Curves from aluminium rectifier.
78. **Wright and Thompson.**
Phil. Mag., (5), **19**, 27, 116, 203. — Position of aluminium in the voltaic series.
79. **Wöhler und Buff.**
Lieb. Ann., **103**, 218 (1858). — Chemistry of aluminium anode.
80. **Zimmermann.**
Trans. Am. Electrochem. Soc., **5**, 147 (1904). — Aluminium condenser.
81. **Zimmermann.**
Trans. Am. Electrochem. Soc., **7**, 309 (1905). — Aluminium condenser.

